

AD-A279 792



DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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ation is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this reducing this burden to: Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson 12 and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

2. REPORT DATE
6 May 19943. REPORT TYPE AND DATES COVERED
Technical Report

4. TITLE AND SUBTITLE

Structure of Di[bis(diethyldithiocarbamato) Zinc (II)]
[μ -bis(Diethylphosphino)ethane] • 2 Toluene

5. FUNDING NUMBERS

N00014-91-J-1258
Matsyn---01

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REPORT NUMBER

Technical Report No. 14

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Dr. H. Guard and Dr. L. Kabikoff
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-500010. SPONSORING / MONITORING
AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

DTIC
ELECTE
S MAY 23 1994 B D

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approval for public release; distribution unlimited

12b. DISTRIBUTION CODE

N00179

13. ABSTRACT (Maximum 200 words)

Di[bis(diethyldithiocarbamato)Zinc(II)][μ -bis(Diethylphosphino)ethane] • 2 Toluene
(et_2NCSS) $_2\text{Zn}$]2 (μ -depe) • 2C₇H₈ Mr = 1114.4, monoclinic, $P 2_1/c$, $a = 12.960(1)$, $b = 11.311(2)$,
 $c = 20.129(5)$, $\beta = 96.46(1)^\circ$, $V = 2932 \text{ \AA}^3$, $Z = 2$, $D_x = 1.254 \text{ g cm}^{-3}$, $\lambda(\text{MoK}\alpha) = 0.070930 \text{ \AA}$,
graphite monochromator, $\mu = 11.89 \text{ cm}^{-1}$, $F(000) = 1180$, $T = 298 \text{ K}$, final $R = 0.055$ ($R_w = 0.072$)
for 2531 observed [$I > 3\sigma(I)$] reflections. The molecule is positioned symmetrically about an
inversion center at the cell origin, which is situated in the center of the bridging diphosphine
ligand. Toluene is disordered in this structure such that the rotation between the two positions of the
methyl carbon is 36° . The geometry about the zinc can be described as distorted trigonal bipyramid.
The Zn- P distance is 2.388 \AA and the zinc-sulphur distances range from 2.320 to 2.653 \AA .

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION
OF REPORT
Unclassified18. SECURITY CLASSIFICATION
OF THIS PAGE
Unclassified19. SECURITY CLASSIFICATION
OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

94 3 20 145

Standard Form 298 (Rev. 2-8)
Prescribed by ANSI Std. Z39-18
298-102

OFFICE OF NAVAL RESEARCH

GRANT N00014-91-J-1258

R&T Code Matsyn---01

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**Structure of Di[bis(diethyldithiocarbamato) Zinc(II)]
[μ - bis(Diethylphosphino)ethane] · 2 Toluene**

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Abstract. Di[bis(diethyldithiocarbamato)Zinc(II)][μ - bis(Diethylphosphino)ethane] · 2 Toluene, [(Et₂NCSS)₂Zn]₂ (μ - depe) · 2C₇H₈ Mr = 1114.4, monoclinic, *P* 2₁/c, *a* = 12.960(1), *b* = 11.311(2), *c* = 20.129(5), β = 96.46(1)°, *V* = 2932 Å³, *Z* = 2, *D*_x = 1.254 g cm⁻³, λ (MoK α) = 0.70930 Å, graphite monochromator, μ = 11.89 cm⁻¹, *F*(000) = 1180, *T* = 298 K, final *R* = 0.055 (*R*_w = 0.072) for 2531 observed [*I* > 3 σ (*I*)] reflections. The molecule is positioned symmetrically about an inversion center at the cell origin, which is situated in the center of the bridging diphosphine ligand. Toluene is disordered in this structure such that the rotation between the two positions of the methyl carbon is 36°. The geometry about the zinc can be described as a distorted trigonal bipyramid. The Zn- P distance is 2.388 Å and the zinc- sulphur distances range from 2.320 to 2.653 Å.

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Experimental. Single crystals of suitable quality for data collection were recrystallized from a toluene solution. The synthesis of this compound is described elsewhere (Zeng & Hampden-Smith). A colorless needle having the dimensions 0.2 x 0.2 x 0.4 mm was mounted in a 0.2 mm diameter sealed capillary tube containing mother liquor to prevent decomposition through loss of solvent. Rapid loss of solvated toluene otherwise occurs in open atmosphere. Cell dimensions were obtained by centering 45 reflections several times ($11 < 2\theta < 27^\circ$). A quadrant of the reciprocal sphere with $h = 0 - 14$, $k = 0 - 12$, $l = \pm 0 - 22$, was collected by $\theta - 2\theta$ ($2\theta_{\max} = 45^\circ$) scans using a Kuma KM-4 diffractometer. Crystal decay was measured by monitoring 2 reflections every 50 data collected and showed a 40% decline in intensity. Corrections for absorption were made modeling a sphere having a radius of 0.1 mm (min. /max. correction = 0.8375/ 0.8380). Zinc was located using standard Patterson methods and the remaining atoms were found through successive difference fourier calculations. Iterative refinement of atomic positions and anisotropic thermal ellipsoids for all atoms except the disordered toluene, which was modeled with isotropic thermal factors, was performed using (GSAS) General Structure Analysis System (Larson & Von Dreele, 1990). Two toluene rings were modeled as rigid bodies with two positions for each carbon. All ring angles were constrained to be 120° and one methyl C-C and only one ring C-C distance were allowed to refine for both rigid bodies. The rotation angle between the two methyl groups refined to $-35.98(0.56)^\circ$. The sum of the occupancies for the rings was fixed at 1.0, with final values of 0.454(24) and 0.546(24) for each ring. The function minimized was $\chi^2 = w[F_o - F_c]^2$, with $w = (2F_o/\sigma F_o^2)^2$, where final residuals at convergence were $R = 0.055$ and $wR = 0.072$ and the last $\sum \Delta/\sigma = 0.0$. There were 232 variables refined for the 2531 observed [$I > 3\sigma(I)$] reflections. Hydrogen atoms were not placed. No correction for extinction was made. The sum of all rho values in a final fourier map was 0.292 electrons. Scattering factors were taken from the *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic positions and equivalent isotropic thermal factors are listed in Table 1, while selected distances and angles are shown in Table 2. Figure 1 presents an ORTEP (Johnson, 1976) drawing of the zinc compound.* Figure 2 is a packing diagram showing the relationship between the zinc complexes and the associated solvent molecules. Only one toluene ring is shown in this diagram for purposes of clarity.

Related Literature. The structure of the title compound (I) shows some similarity to that of the parent dimer (II), Bis(diethyldithiocarbamato) zinc(II) (Bonamico, Mazzone, Vaciago & Zambonelli, 1965). In the latter, one dithiocarbamate ligand bridges both zinc atoms of this dimeric complex, while the other type chelates to each Zn(II). A five coordinate, distorted

trigonal bipyramid environment for zinc results from the long (2.81 Å) sulphur bridge. The inversion center of the monoclinic cell lies in the center of the zinc dimer (II) between the bridging dithiocarbamate ligands. Upon introducing the diphosphine ligand, an expansion of the monoclinic cell is observed with a contraction of the beta angle. However the symmetry of the cell remains the same, $P 2_1/c$. Both dithiocarbamate ligands become chelating, whereupon the diphosphine bridges the zinc atoms and the inversion center lies between the phosphorous atoms. In the title complex, (I), the zinc coordination geometry remains similar to the parent compound and can be similarly represented by a distorted trigonal bipyramid.

* Lists of structure factors, anisotropic thermal parameters and a complete table of bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. . Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference:]

Acknowledgment. MJH-S and DZ thank the office of Naval Research, Chemistry and Materials Research division for funding and the NSF Chemical Instrumentation program for the purchase of a Low-Field NMR spectrometer.

References

BONAMICO, M., MAZZONE, G., VACIAGO, A. & ZAMBONELLI, L. (1965). *Acta Cryst.* 19, pp. 898-909.

JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL- 5138. Oak Ridge National Laboratory, Tennessee, USA

LARSON, A.C. & VON DREELE, R. B. (1990). *GSAS, General Structure Analysis System*, Report LAUR 86- 748. Los Alamos National Laboratory, New Mexico, USA

ZENG, D. & HAMPDEN- SMITH, M. J., *Inorg. Chem.*, In preparation

Table 1. Atomic Positions in Fractional Coordinates

Name	X	Y	Z	U _i /U _e *100
Zn	0.22228(8)	0.00208(10)	0.13061(5)	5.51*
P	0.17153(17)	0.02645(21)	0.01365(11)	5.02*
C1	0.0435(6)	-0.0315(8)	-0.0161(4)	5.09*
C2	0.2550(7)	-0.0581(11)	-0.0388(5)	8.24*
C3	0.3684(8)	-0.0224(14)	-0.0233(6)	11.61*
C4	0.1716(8)	0.1807(9)	-0.0133(5)	8.02*
C5	0.1379(10)	0.2026(11)	-0.0867(6)	11.08*
S1a	0.23159(21)	-0.23105(22)	0.11772(14)	7.11*
S2a	0.10560(20)	-0.08128(21)	0.19647(12)	6.14*
N1a	0.0920(6)	-0.3153(7)	0.1942(4)	7.16*
C1a	0.1387(7)	-0.2208(8)	0.1716(4)	5.85*
C2a	0.1226(10)	-0.4379(10)	0.1746(6)	9.95*
C3a	0.0514(11)	-0.4788(10)	0.1117(8)	12.98*
C4a	0.0120(8)	-0.3035(10)	0.2408(5)	7.85*
C5a	0.0646(9)	-0.3083(12)	0.3132(5)	10.21*
S1b	0.22282(20)	0.22095(22)	0.16682(14)	6.53*
S2b	0.39220(18)	0.04896(22)	0.17197(13)	6.22*
N1b	0.4174(6)	0.2693(7)	0.2147(4)	6.44*
C1b	0.3506(7)	0.1890(8)	0.1871(4)	5.22*
C2b	0.3853(8)	0.3953(8)	0.2228(6)	7.95*
C3b	0.3409(9)	0.4126(10)	0.2896(6)	9.37*
C4b	0.5267(7)	0.2399(9)	0.2422(6)	8.01*
C5b	0.5968(9)	0.2621(10)	0.1909(7)	10.88*
C1t	0.2399(7)	-0.0356(9)	0.4203(10)	15.1(14)
C1't	0.2560(9)	-0.0097(11)	0.3823(6)	12.7(10)
C2t	0.3621(10)	0.0704(12)	0.4995(5)	10.3(10)
C2't	0.3124(9)	0.0192(10)	0.5006(5)	11.3(9)
C3t	0.2801(11)	-0.0105(11)	0.4865(7)	15.4(15)
C3't	0.2465(7)	-0.0358(9)	0.4495(7)	12.2(10)
C4t	0.2817(11)	0.0202(13)	0.3670(6)	12.8(12)
C4't	0.3313(10)	0.0714(11)	0.3660(4)	11.1(9)
C5t	0.4039(7)	0.1262(7)	0.4462(8)	13.8(13)
C5't	0.3877(7)	0.1004(8)	0.4843(5)	9.6(8)
C6t	0.4831(15)	0.2043(16)	0.4587(17)	17.7(20)
C6't	0.4512(15)	0.1535(16)	0.5335(11)	13.4(13)
C7t	0.3637(11)	0.1311(12)	0.3800(6)	12.6(12)
C7't	0.3972(8)	0.1264(8)	0.4170(6)	10.8(9)

* U_e = 1/3 Σ u₁₁+u₂₂+u₃₃

Table 2. Selected Distances (Å) and Angles(°).

Zn- P	2.388(2)	Zn- P- C1	115.01(27)
		Zn- P- C2	112.77(35)
		Zn- P- C4	113.16(33)
		C1- P- C2	101.2(4)
P- C1	1.822(8)		
C1- C1 ⁱ	1.537(16)	C1- P- C4	106.1(4)
P- C2	1.859(10)	C2- P- C4	107.6(5)
C2- C3	1.522(14)		
P- C4	1.827(10)		
C4- C5	1.514(14)		
Zn- S1a	2.653(2)	P- Zn- S1a	91.65(9)
Zn- S2a	2.320(2)	P- Zn- S2a	119.03(9)
		S1a- Zn- S2a	72.05(8)
		S1a- Zn- S1b	169.17(10)
		S1a- Zn- S2b	102.11(9)
S1a- C1a	1.712(9)	Zn- S1a- C1a	80.07(33)
S2a- C1a	1.724(9)	Zn- S2a- C1a	90.36(31)
C1a- N1a	1.334(10)	S1a- C1a- N1a	122.7(7)
S1a- S2a	2.937(3)	S2a- C1a- N1a	119.8(8)
		S1a- C1a- S2a	117.5(5)
N1a- C2a	1.506(13)		
C2a- C3a	1.551(17)		
N1a- C4a	1.480(12)		
C4a- C5a	1.538(14)		
Zn- S1b	2.580(2)	P- Zn- S1b	99.17(9)
Zn- S2b	2.326(2)	P- Zn- S2b	118.11(9)
		S1b- Zn- S2b	73.01(9)
		S2a- Zn- S1b	102.10(9)
		S2a- Zn- S2b	122.66(10)
S1b- C1b	1.699(9)	Zn- S1b- C1b	80.54(31)
S2b- C1b	1.712(9)	Zn- S2b- C1b	88.29(30)
C1b- N1b	1.332(10)	S1b- C1b- N1b	121.7(7)
S1b- S2b	2.926(3)	S2b- C1b- N1b	120.1(7)
		S1b- C1b- S2b	118.2(5)
N1b- C2b	1.498(11)		
C2b- C3b	1.533(14)		
N1b- C4b	1.499(11)		
C4b- C5b	1.472(15)		

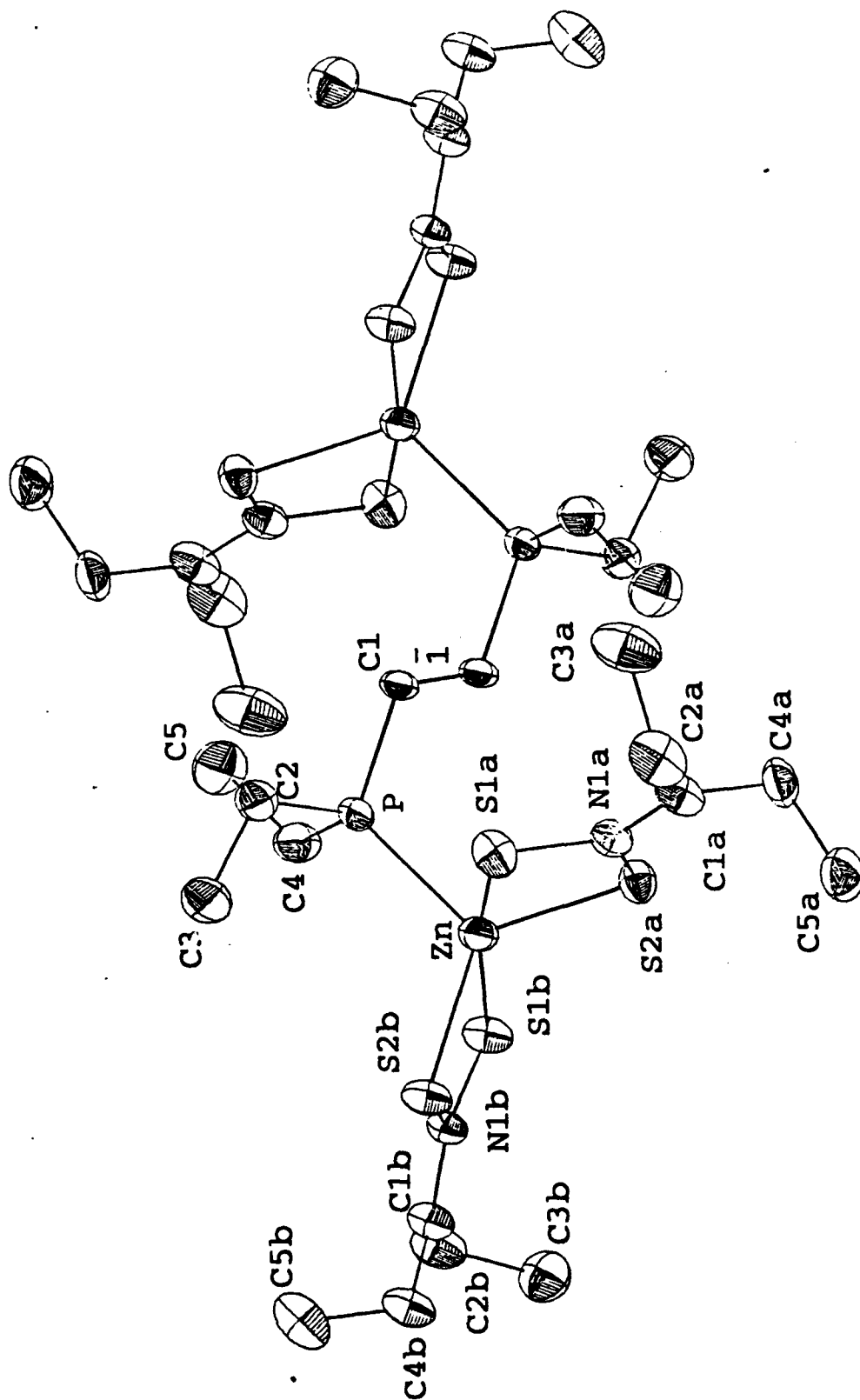
Toluene Rings

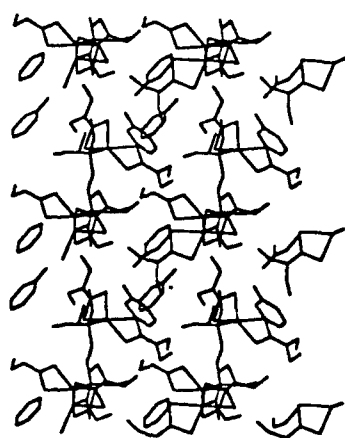
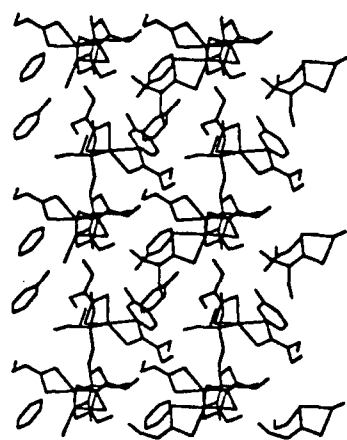
C ring- C methyl	1.35(2)
C ring- C ring	1.404(4)
All angles constrained to 120°	

Figure Captions

Figure 1. An ORTEP representation of the zinc dimer. Each half of the molecule is related to the other by the inversion center.

Figure 2. A stereo diagram of the packing arrangement in the crystal structure.





Supplimentary Information

- 1. Anisotropic Thermal Parameters**
- 2. Full Listing of Distances and Angles.**
- 3. Listing of Calculated and Observed Structure Factors.**